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Synthesis of Benzo[1,2-*b*:4,5-*b'*]dithiophene and its 4,8-Dimethoxy and 4,8-Dimethyl Derivatives

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Synthese von Benzo[1,2-*b*:4,5-*b'*]dithiophen und seinen 4,8-Dimethoxy- und 4,8-Dimethyl-Derivaten

Eine einfache Synthese für Benzo[1,2-*b*:4,5-*b'*]dithiophen (**4**) und die Synthese seines bisher unbekannten 4,8-Dimethoxy- (**7**) und 4,8-Dimethylderivates (**13**) wird beschrieben. IR-, ^{1}H-NMR-, UV- und MS-Daten werden mitgeteilt.

In our group a large number of polyheteroarylenealkenylenes[1] with thiophene units were synthesized and their electrical conducting properties studied. In connection with this work, we also became interested in using condensed thiophene systems as units for such polymers[2]. We therefore prepared the benzo[1,2-*b*:4,5-*b'*]dithiophene system **4** and two of its derivatives.

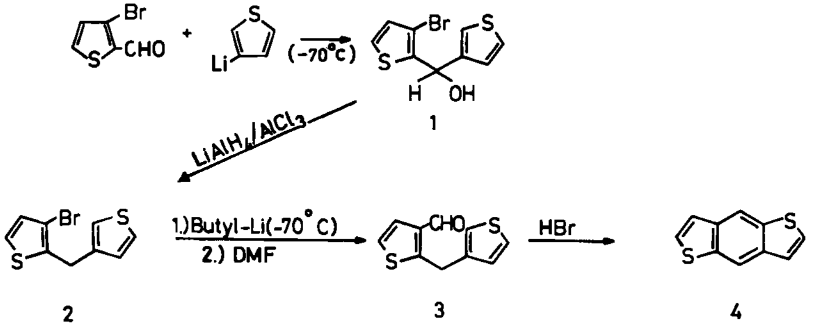
Results and Discussion

Benzo[1,2-*b*:4,5-*b'*]dithiophene (4)

Two synthetic routes are described[3,4] for preparing the system **4**. The synthesis described by *Rao* and *Tilak*[3] could not be reproduced and the method of *Dann* and *Kokorudz*[4] leads to a complex mixture of products as can easily be seen by the ^{1}H NMR spectrum.

We prepared benzo[1,2-*b*:4,5-*b'*]dithiophene (**4**) as shown in Scheme 1, using the cyclisation reaction described by *Wynberg* et al.[5] for the synthesis of isomeric benzo[1,2-*b*:5,4-*b'*]dithiophene.

Scheme 1



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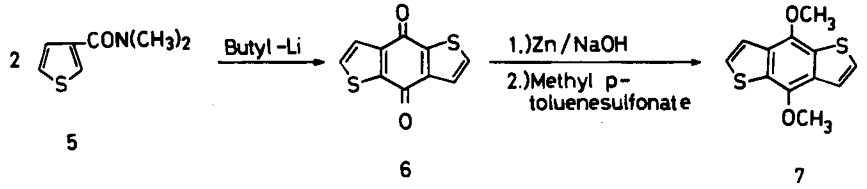
4,8-Dimethoxybenzo[1,2-*b*:4,5-*b'*]dithiophene (7)

The unknown 4,8-dimethoxy derivative **7** was prepared from dione **6**[6] by the reaction with Zn/NaOH and methylation with methyl *p*-toluenesulfonate as shown in Scheme 2 analogous to the preparation of 9,10-dimethoxyanthracene[7] from anthraquinone.

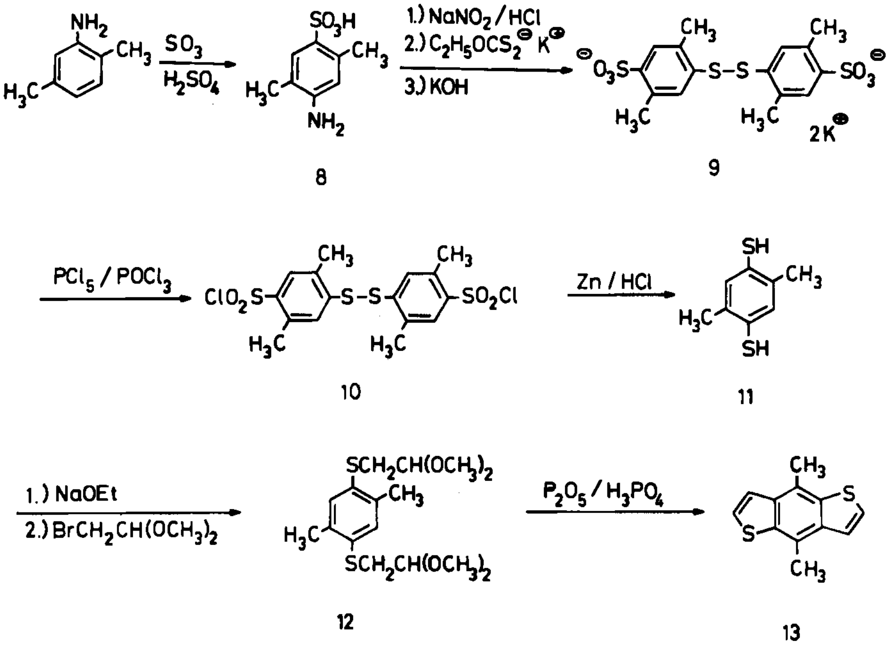
Scheme 2



4,8-Dimethylbenzo[1,2-*b*:4,5-*b'*]dithiophene (13)

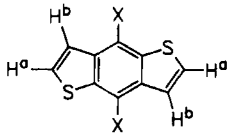
The 4,8-dimethyl derivative **13** was obtained as shown in Scheme 3, according to the method described by *Rao* and *Tilak*[3] for the unsubstituted system.

Scheme 3



The structures of the compounds described in this paper were confirmed by elemental analysis and spectroscopic methods. The ^1H NMR spectra show typical doublets of the AB spin system of the condensed thiophene rings with coupling constants of about 5 to 5.5 Hz. NMR data are given in Table 1. The UV spectra show the expected effects of substitution as shown in Table 2. For results of the IR and mass spectra see experimental section.

Table 1. Chemical shifts δ[ppm] and coupling constants [Hz] in the ^1H NMR spectra of **4**, **7**, and **13** (solvent acetone)



	Structure	δ_a(d)	δ_b(d)	δ_x(s)	J_{ab}
4	X = H	7.72	7.51	8.49	5.5
7	X = OCH_3	7.68	7.60	4.14	5
13	X = CH_3	7.68	7.61	2.77	5.5

Table 2. UV absorption maxima λ_{max} (log ε) of **4**, **7**, and **13** in ethanol (sh = shoulder)

	4		**7**		**13**	
X =	H		OCH_3		CH_3	
	235 (sh)	(4.31)	226	(4.44)	226.5	(4.38)
	239 (sh)	(4.36)	246	(4.51)	246	(4.55)
	247.5	(4.60)	253	(4.66)	253	(4.68)
	256	(4.74)	275 (sh)	(3.57)	276.5 (sh)	(3.64)
	291	(3.75)	285	(3.78)	287	(3.91)
	301	(3.81)	298	(3.79)	298.5	(4.02)
	321	(3.84)	318 (sh)	(3.50)	315 (sh)	(3.54)
	326	(3.79)	333	(3.93)	328.5	(3.98)
	334	(4.05)	347.5	(4.10)	343	(4.19)

Experimental

Melting points: Kofler hot stage microscope. – IR spectra: Perkin Elmer 580 B spectrometer, recorded by an Infrared Data Station 3500. – Mass spectra: Varian MAT 711; only significant peaks are reported; exact mass measurements: resolution 10000–30000 (10% relative valley definition). – ^1H NMR spectra: Bruker WH 270 or Varian XL 100, tetramethylsilane internal standard. – UV spectra: Beckman Acta M VI spectrophotometer. – Elemental analyses: Microanalytical laboratory of our institute.

3-Bromo-α-(3-thienyl)-2-thiophenemethanol (**1**): 68.5 g (0.42 mol) of 3-bromothiophene[8] was metalated with butyllithium (2.25 N in hexane) at –70°C. Treatment with 79.5 g (0.42 mol) of 3-bromo-2-thiophenecarboxaldehyde[9] yielded 111 g (97%) of **1**[10] as an orange-red oil, which was used without further purification. Purification of a small portion by repeated short-path distillation (0.1 mbar) was unsuccessful (decomp. 200°C). – ^1H NMR/100 MHz (CCl_4): δ = 3.25 (1 H, OH), 6.0 (s, 1 H, methine), 6.75–7.15 (5 H, thiophene).

3-Bromo-2-(3-thienylmethyl)thiophene (**2**): 99 g (0.36 mol) of unpurified **1** was reduced with $LiAlH_4/AlCl_3$ mixture[11] to give 67.4 g (72%) of **2** as yellow oil after distillation i. vac.; b.p. 110–118°C/0.5 mbar, n_D^{20} = 1.6302 (Lit.[10] b.p. 102–106°C/0.2 mbar, n_D^{20} = 1.6363). A small portion was redistilled by repeated short-path distillation (130°C/0.3 mbar) to obtain **2** as a colourless liquid of n_D^{20} = 1.6242. – ^1H NMR/100 MHz (CCl_4): δ = 3.99 (s, 2 H, CH_2), 6.7–7.1 (5 H, thiophene).

2-(3-Thienylmethyl)-3-thiophenecarboxaldehyde (**3**): 133 ml of butyllithium (2.25 N in hexane) and 70 ml of dry ether were cooled to −70°C under nitrogen. A solution of 65 g (0.25 mol) of **2** in 250 ml of dry ether was also cooled to −70°C and added in drops under continuous stirring. After 10 min of stirring at −70°C the yellow solution was poured into a well stirred mixture of 36.5 g (0.50 mol) of absol. DMF and 200 ml of dry ether, by means of nitrogen pressure. The colour changed to deep blue. The mixture was stirred for 2 h at room temp. and left standing about 12 h. During this time the colour turned green. After hydrolysing with 500 ml of ice water the organic layer was separated, extracted twice with 2 N HCl, and washed with water, sat. $NaHCO_3$ solution, and water until neutral. The organic phase was dried over $MgSO_4$ and evaporated leaving 52 g (99%) of red viscous oil. A sample was distilled by repeated short-path distillation (130°C/0.1 mbar), but could not be separated from the impurity of the starting material **2**, n_D^{20} = 1.6155. – IR (KBr): 3100 (aromat. CH), 2950, 2920 (aliphat. CH), 2850, 2735 (CHO), 1670 cm^{-1} (C=O). – ^1H NMR/100 MHz (CCl_4): δ = 4.45 (s, 2H, CH_2), 6.8 – 7.35 (5H, aromat. H), 9.95 (s, 1H, CHO).

2,4-Dinitrophenylhydrazone: M.p. 195 – 196°C from glacial acetic acid. – IR (KBr): 3290, 3270 (NH), 3100 (aromat. CH), 1615 (C=N), 1515, 1332 cm^{-1} (NO_2).

$C_{16}H_{12}N_4O_4S_2$ (388.4) Calcd. C 49.48 H 3.11 N 14.42 S 16.51
Found C 49.22 H 3.34 N 14.29 S 16.47

Benzo[1,2-b:4,5-b']dithiophene (**4**): 50 g of crude aldehyde **3** was refluxed with 250 ml of 48% hydrobromic acid for 2.5 h. The resulting black tar-like material was removed by filtration, washed with water, and dried i. vac. at 50°C (KOH). The crude product was sublimed i. vac. at 130°C yielding 20 g of a nearly white substance. After recrystallisation from ethanol 17.9 g (39%) of analytical pure **4** was obtained as colourless plates, m.p. 197.5 – 198°C (Lit.[3] 198°C). – IR (KBr): 3100, 3075, 1730, 1512, 1445, 1388, 1324, 1292, 1178, 1080, 1054, 890, 864, 835, 785, 737, 648, 474 and 413 cm^{-1}. – MS: *m/z* 189.99125 (calcd. 189.99110) ($C_{10}H_6S_2$, M^+, 100%), 191 ($[M+1]^+$, 13), 192 ($[M+2]^+$, 11), 145 ($[M-CHS]^+$, 11), 102 ($[C_8H_6]^+$, 4), 95 (M^{2+}, 7).

$C_{10}H_6S_2$ (190.3) Calcd. C 63.12 H 3.18 S 33.70 Found C 63.18 H 3.22 S 33.75

N,N-Dimethyl-3-thiophenecarboxamide (**5**): 80.3 g (0.55 mol) of 3-thiophenecarbonyl chloride[12,13] was converted into **5** as described[6] using gaseous dimethylamine instead of aqueous solution, which increases the yield of **5** from 45 to 91% (77.5 g) after distillation in vacuo (b.p. 95°C/0.7 mbar).

Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (**6**): 345 ml of butyllithium (1.66 N in hexane) was dropped into the solution of 77.5 g (0.50 mol) of **5** in 1400 ml of dry ether during continuous stirring under dry nitrogen. After 10 min a light yellow precipitate was formed and the mixture stirred for about 12 h. After addition of ice water, the amorphous precipitate of quinone **6** was recrystallized from glacial acetic acid. 30.6 g (56%) of olive green coloured microcristalline product was obtained, m.p. 260 – 262°C (Lit.[6,14] 258 – 260°C). – ^1H NMR/170 MHz ($[^2H_6]DMSO$): δ = 8.17 (d, 2H, H^2 and H^6), 7.66 (d, 2H, H^3 and H^7, $J_{23} = J_{67}$ = 6 Hz).

4,8-Dimethoxybenzo[1,2-b:4,5-b']dithiophene (**7**): 10 g (45 mmol) of quinone **6** was ground with 6.5 g (0.10 mol) of zinc dust and placed in a reaction flask with 20 ml of ethanol. 150 ml of 20% NaOH was added and the mixture refluxed for 1 h until most of the quinone was brought into the solution. Methyl *p*-toluenesulfonate was then added in small portions (about 40 ml) with stirring continually until the colour changed to red. The resulting precipitate was filtered and extracted with boiling $Na_2S_2O_5$ solution for three times. The remaining yellow crystals were dissolved in benzene, the solution filtered from excess zinc dust, and the benzene removed i. vac. leaving 7.9 g of crude product which was purified by sublimation (140°C/0.1 mbar). Yield 7.2 g (63%), light yellow crystals, m.p. 148–149°C. – IR (KBr): 3110, 3090, 2995, 2970, 2935, 2830, 1515, 1456, 1420, 1363, 1203, 1170, 1026, 922, 890, 811, 745, 696, 665, 637, 512, 461 cm^{-1}. – MS: *m/z* 250.01227 (calcd. 250.01223) ($C_{12}H_{10}O_2S_2$, M^+, 48%), 251 ($[M + 1]^+$, 7), 252 ($[M + 2]^+$, 5), 235 ($[M - CH_3]^+$, 100), 220 ($[M - 2CH_3]^+$, 12), 192 ($[M - 2CH_3, - CO]^+$, 14), 125 (M^{2+}, 29), 111 ($C_5H_3OS^+$, 8).

$C_{12}H_{10}O_2S_2$ (250.3) Calcd. C 57.58 H 4.03 S 25.62 Found C 57.78 H 3.97 S 25.45

4-Amino-2,5-dimethylbenzenesulfonic Acid (**8**): 121 g (1.00 mol) of 2,5-dimethylaniline was slowly poured into 480 g of strongly cooled oleum (20% SO_3). The mixture was heated to 170–180°C in an oil bath for 2 h, cooled, and poured onto ice. The precipitated sulfonic acid was purified via its sodium salt, yielding 163 g (81%).

Dipotassium 4,4'-Dithiobis(2,5-dimethylbenzenesulfonate) (**9**): The solution of 163 g (0.81 mol) of sulfonic acid **8** in 3.3 l of 0.25 N Na_2CO_3 was cooled to 0–5°C and 825 mol of 1 N $NaNO_2$ was added. Under stirring, a mixture of 660 ml of ice water and 660 ml of conc. HCl was added at such a rate as to keep the temperature below 5°C. The mixture was stirred for 1 h and the precipitated diazonium salt removed by suction filtration and suspended in 200 ml of water. This suspension was added in portions to a well stirred solution of 132 g (0.83 mol) of potassium *O*-ethylxanthogenate, which was heated to 70°C on a steam bath. After the vehement reaction was complete 330 g of KOH was added and the mixture refluxed for 3 h. It was then cooled in an ice bath and acidified with half concentrated HCl. The precipitate formed was filtered off, recrystallized from water, and dried i. vac. Yield 128 g (62%) of white substance, which did not melt up to 360°C.

4,4'-Dithiobis(2,5-dimethylbenzenesulfonyl Chloride) (**10**): 128 g (0.25 mol) of **9**, 190 g (1.24 mol) of $POCl_3$, and 32 g (0.15 mol) of PCl_5 were heated under reflux for 6 h and poured onto ice. The precipitate formed was filtered off and dried, yielding 95 g (80%) of crude **10**, m.p. 166–169°C (decomp.). – The analytical sample was recrystallized from benzene/petrol ether.

$C_{16}H_{16}Cl_2O_4S_4$ (471.5) Calcd. C 40.76 H 3.42 Cl 15.04 S 27.20
Found C 41.28 H 3.61 Cl 14.99 S 27.01

2,5-Dimethyl-1,4-benzenedithiol (**11**): 94 g (0.20 mol) of **10** and 480 g of zinc dust were suspended in 1.9 l of ethanol. The suspension was cooled in an ice bath. 925 ml of conc. HCl was added in drops over a period of 1.5 h and the mixture stirred at room temp. for additional 2 h. It was then heated under reflux for 2 h and the ethanol removed by distillation. 1 l of water was added to the residue and the mixture steam distilled in small portions and approximately 100 ml of conc. HCl was added per portion. The crystalline material obtained was dissolved in ether and the combined ether extracts dried over $MgSO_4$. Evaporation of the ether left 33 g (46%) of product, m.p. 123–124°C. A run of 50 g of **10** yields 21.2 g (59%). The analytical sample was sublimed in vacuo. – IR (KBr): 2985 (aromat. CH), 2940 and 2860 (aliphat. CH), 2565 and 2545 cm^{-1} (SH). – ^1H NMR/270 MHz ($CDCl_3$): $\delta = 7.10$ (s, 2H, aromat. H), 3.20 (s, 2H, SH), 2.24 (s, 6H, CH_3).

$C_8H_{10}S_2$ (170.3) Calcd. C 56.42 H 5.92 S 37.66 Found C 56.70 H 6.22 S 37.80

1,4-Bis(2,2-dimethoxyethylthio)-2,5-dimethylbenzene (**12**): 32 g (0.19 mol) of **11** was dissolved under stirring in sodium methoxide (prepared from 8.9 g of Na and 160 ml of absol. ethanol). 64 g (0.38 mol) of bromoacetaldehyde dimethyl acetal was added and the mixture heated under reflux for 3 h. Most of the ethanol was evaporated and the residue diluted with water. The precipitate formed was removed by suction filtration, washed with water, and dried i. vac. yielding 62.7 g (96%), m.p. 72–73 °C. The analytical sample was recrystallized from benzene/petrol ether.

$C_{16}H_{26}O_4S_2$ (346.5) Calcd. C 55.46 H 7.56 S 18.51 Found C 55.71 H 7.48 S 18.84

4,8-Dimethylbenzo[1,2-b:4,5-b']dithiophene (**13**): 39 g (0.11 mol) of **12** was dissolved in 350 ml of xylene. 20 ml of H_3PO_4 and 2 g of P_2O_5 were added and the mixture heated on a water separator for 5 h to remove methanol and water. After cooling, the solution was decanted from the phosphorous acid mixture, washed with a little water, and dried. Filtration and evaporation of the solvent left a crude product which was sublimed i. vac. (130 °C/0.1 mbar) yielding 17 g (69%) of analytical pure **13** as colourless crystalline substance of m.p. 164 °C (Lit.[15] 169 °C). – IR (KBr): 3100, 3080, 2915, 2855, 1723, 1616, 1563, 1504, 1438, 1384, 1297, 1193, 1091, 1024, 913, 879, 800, 746, 640, 450 cm^{-1}. – MS: *m/z* 218.02239 (calcd. 218.02240) ($C_{12}H_{10}S_2$, M^+, 100%), 219 ($[M+1]^+$, 15), 220 ($[M+2]^+$, 8), 203 ($[M-CH_3]^+$, 18), 109 (M^{2+}, 6).

$C_{12}H_{10}S_2$ (218.3) Calcd. C 66.01 H 4.62 S 29.37 Found C 66.23 H 4.64 S 29.44

CAS Registry Numbers

1: 17964-88-4 / **2**: 17965-56-9 / **3**: 72771-52-9 / **3** (DNP hydrazone): 104033-90-1 / **4**: 267-65-2 / **5**: 59906-37-5 / **6**: 32281-36-0 / **7**: 85903-02-2 / **8**: 27897-08-1 / **9**: 104014-84-8 / **10**: 104014-85-9 / **11**: 104014-86-0 / **12**: 104014-87-1 / **13**: 15888-29-6 / 3-bromothiophene: 872-31-1 / 3-bromo-2-thiophenecarboxaldehyde: 930-96-1 / 3-thiophenecarbonyl chloride: 41507-35-1 / 2,5-dimethylaniline: 95-78-3 /potassium *O*-ethylxanthogenate: 140-89-6 / bromoacetaldehyde dimethyl acetal: 7252-83-7

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